Title: Nuclear Forensics and Radiochemistry: Chemistry

Author(s):   Rundberg, Robert S.

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Nuclear Forensics and Radiochemistry: Chemistry
Robert S. Rundberg

Abstract:

The chemical behavior of radioactive elements can differ from conventional wisdom because the number of atoms can be unusually small. Kinetic effects and unusual oxidation states are phenomena that make radiochemistry different from conventional analytic chemistry. The procedures developed at Los Alamos are designed to minimize these effects and provide reproducible results over a wide range of sample types. The analysis of nuclear debris has the additional complication of chemical fractionation and the incorporation of environmental contaminants. These are dealt with through the use of three component isotope ratios and the use of appropriate end members.

Nuclear Forensics and Radiochemistry: Chemistry

Lecture 6

Forensics of a nuclear blast

If an atomic bomb were to detonate in a U.S. city, nuclear sleuths would use a wide range of tools to puzzle out the nature of the bomb and who was responsible. Each weapon type has a distinct fingerprint encompassing the waveforms it emits and the fallout it unleashes.

Electromagnetic pulse

Light

Gamma rays

Infrasound

Pressure wave

Seismic waves

Nuclear terrorism
The likeliest scenario is an atomic bomb set off on a city street.

Remote sensing
Dedicated military satellites are on a constant vigil for nuclear detonations.

Fallout

Air sampling
Radioxenon and other isotopes can reveal the type of fissile material and bomb design details.

Ground sampling
Fallout constituents and melt glass reveal bomb details and neutron energies.

Sensor network
The new Discreet Oculus sensor array, which records electromagnetic emissions and other waveforms, is being deployed in major U.S. cities.

Radiochemistry
Fallout is a mélange of the vaporized environment—soil and structures that were near the blast—laced with fission products, radioisotopes made in the explosion,, and residual nuclear material.

Post Detonation Debris

- The radiochemical evidence will be in at least two forms
  - Glassy debris i.e., Trinitite
  - Particulate on filter paper flown through the radioactive plume

- Multiple Samples are required to correct for fractionation or environmental contamination
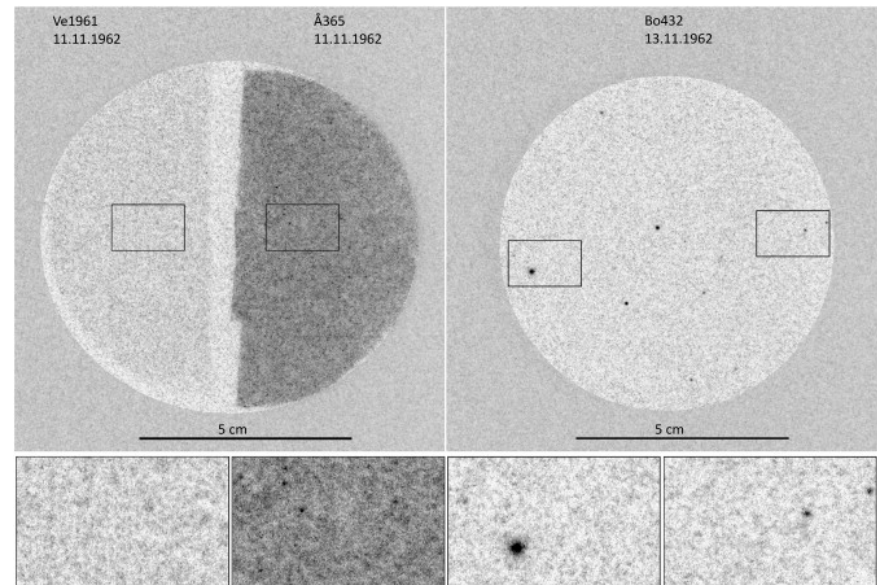
Peculiarities of Radiochemistry

- Carrier free radioactive elements can be a very small number of atoms.
  - A desirable sample of 1e14 fissions per gram has only 6e12 atoms of ^{99}Mo a peak yield isotope
  - A valley isotope ^{111}Ag would be about 2e10 atoms
  - That is less than a micromole. Nano-mole for silver.
- Kinetics can be very slow at these concentrations.
- Depending on the nuclear process of formation the atoms can be in an unusual oxidation state.

Procedure for Dissolving Debris from LA-1721

- Step 1. Place the dried, pulverized sample in a cylindrical Teflon vessel of ~100-ml capacity. Add 25 ml of fuming HNO_3, 100 ml of cone $HClO_4$, and, with care, 50 ml of conc. HF. Heat to strong fumes of $HClO_4$ on a hot plate (medium setting). The solution process may be accelerated by placing an aluminum jacket around the Teflon container.

- Step 2. Cool, add another 50 ml of conc. HF, and again evaporate to strong fumes of $HClO_4$.

- Step 3. Repeat Step 2 twice. (If 10 g of debris are being dissolved, repeat Step 2 four times; add $HClO_4$ as necessary to to prevent the sample from becoming dry.)

- Step 4. Evaporate until the volume is ""50 ml, cool, and add 100 ml of 3M HCl. Warm slightly to dissolve any solids.

- Step 5. Divide the solution among four 40-ml Vycor centrifuge tubes. Wash the Teflon vessel with 3M HCl and add the washes to the centrifuge tubes. Centrifuge for 2 min at 3500 rpm. During the centrifugation wash the Teflon vessel under a stream of H_2O. Rub the inner surfaces well and flush them with H_2O to remove adhering SiO_2 particles, which may be discarded. The vessel is now ready for re-use in the following step.

- Step 6. Transfer the supernate to the clean Teflon vessel, add 50 ml each of conc. HF and $HClO_4$, and begin heating on a hot plate (medium setting).

- Step 7. Wash the precipitates in the centrifuge tubes with 3M HCl, centrifuge, and add the supernates to the Teflon vessel on the hot plate.

- Step 8. To each of the precipitates remaining inthe centrifuge tubes add 2 to 3 ml of 6M N aOH and boil while stirring over a burner. Cool, acidify with 3M HCl, bring to a boil and centrifuge. Combine the supernates with those in the Teflon vessel. If more than a few grains of sand and/or any beta-gamma activity remain, repeat the NaOH-HCl treatment until no sand is left or until it is no longer active. (For complete destruction of solids, repeat the sequence of Steps 2 through 8 until the sand is entirely dissolved.)

- Step 9. Heat the contents of the Teflon vessel to strong fumes of $HClO_4$. Cool, add 50 ml of conc. HF, and evaporate the solution until the volume is ~50 ml. Cool.

- Step 10. Add 100 ml of 3M HCl and warm slightly to dissolve any solid material. Divide the solution among four clean 40-ml Vycor centrifuge tubes and centrifuge at 3500 rpm.

- Step 11. Filter the supernate through polypropylene "paper" into a labeled, graduated plastic bottle. Wash the Teflon vessel and the centrifuge tubes with 3M HCl, centrifuge, and filter the washes into the plastic bottle. If any precipitate remains in the centrifuge tubes, add 2 to 3 ml of 6M NaOH and heat over a burner. Cool, neutralize with 3M HCl, centrifuge, and decant the supernate through the filter into the plastic bottle. Repeat the NaOH-HCl treatment if a precipitate still remains in the centrifuge tubes.

- Step 12. Add 3M HCl to make the concentration of the original sample in solution ≤7.5 mg/ml. Heat the final solution overnight in a water bath at ~90°C. (For reasons that are not at all clear, this heat treatment gives a sample solution that may be analyzed satisfactorily. Without such treatment, results may be erratic.)
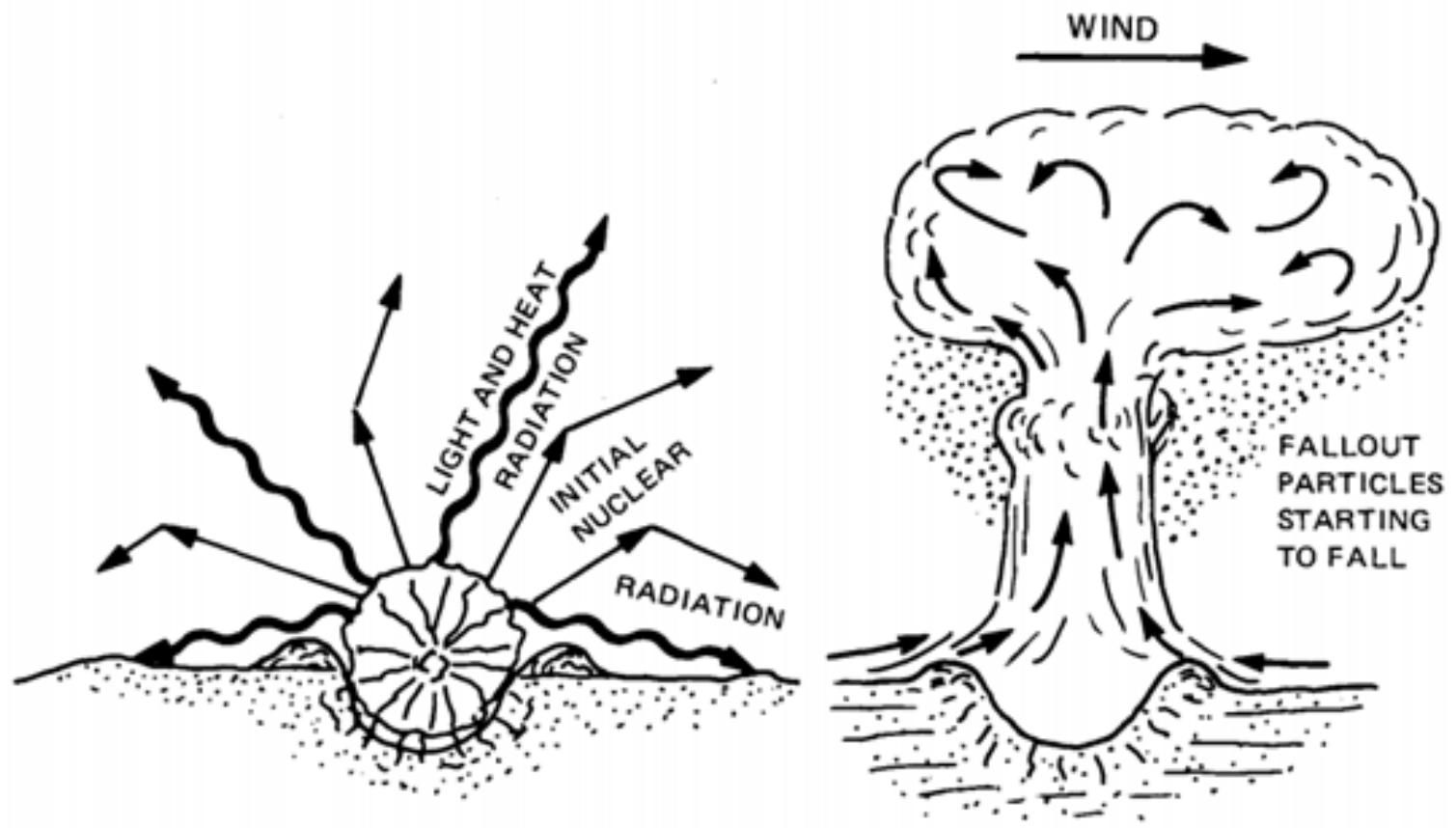
Notes on the Dissolution Procedure

- The use of perchloric acid ensures that the radioactive elements are oxidized to their highest oxidation state.
  - This is important for reproducibility.
  - Some elements will be volatilized and, as a consequence, lost.
- Perchloric acid speeds the removal of silicates because is has a higher boiling point than most acids.
- The final step which involves heating overnight with 3 molar acid is clearly a step to ensure the slow kinetics of ligand formation in some elements is overcome.
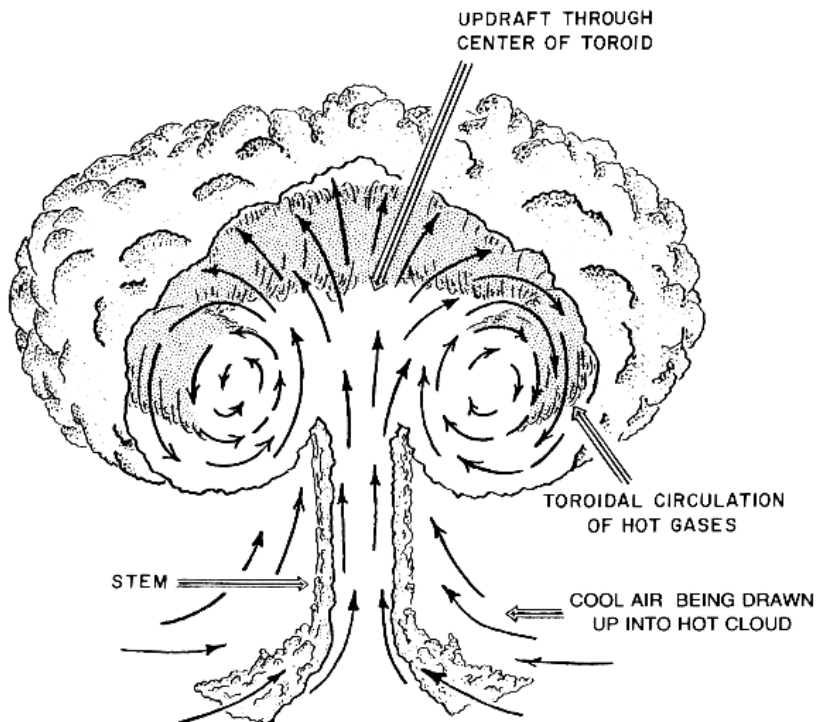
Separation of the Elements

- The procedures described in LA-1721 cover the separation of most of the elements on the periodic chart.
- Every procedure begins with adding 10 to 40 milligrams of carrier.
  - The carrier ensures that chemical separation is reproducible and efficient
- The procedures, while similar to those in qualitative analysis, are designed to be very robust.
  - These procedures have been used on samples from a variety of environmental settings
  - Specific steps have been developed in some cases to remove problematic elements, e.g., iron.

Effects of a Nuclear Explosion

ORNL-DWG 78-6264

WIND

LIGHT AND HEAT RADIATION

INITIAL NUCLEAR RADIATION

FALLOUT PARTICLES STARTING TO FALL

Fractionation

UPDRAFT THROUGH
CENTER OF TOROID

TOROIDAL CIRCULATION
OF HOT GASES

STEM

COOL AIR BEING DRAWN
UP INTO HOT CLOUD

- Atmospheric tests from towers or balloons are not typically fractionated.
- Tests on or near the ground are highly fractionated because material from the soil environment is swept up into the cloud.
- Refractory elements are uniformly incorporated into the first condensing (refractory) material.
- Volatile elements are condensed on the surface of particles as they cool.
- Smaller particles have a higher surface area to mass ratio and therefore have a higher fraction of volatiles.

Fallout Pattern near a Nuclear Explosion

The most hazardous fallout particles are readily visible as fine, sand-sized grains, but the lack of apparent fallout should not be misrepresented to mean radiation isn't present; therefore appropriate radiation monitoring should always be performed.. Fallout that is immediately hazardous to the public and emergency responders will descend to the ground within about 24 hours.
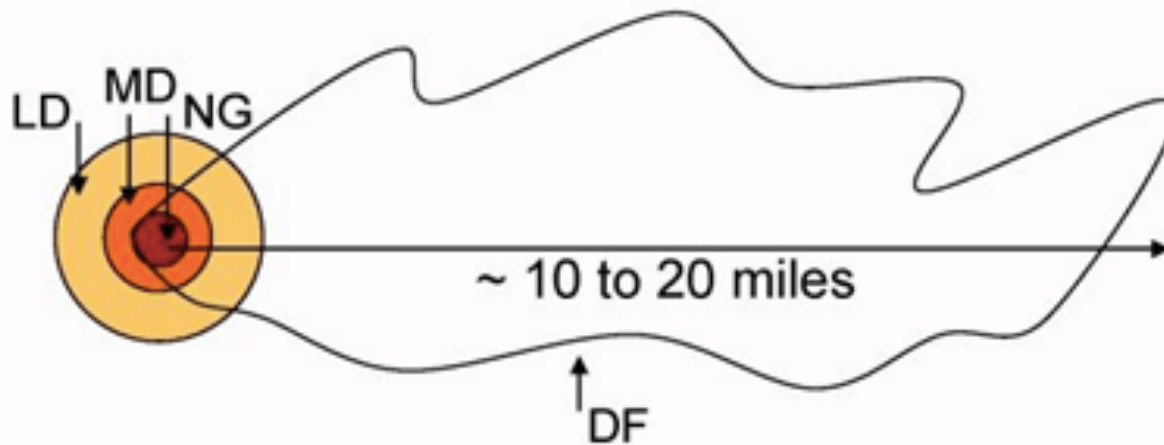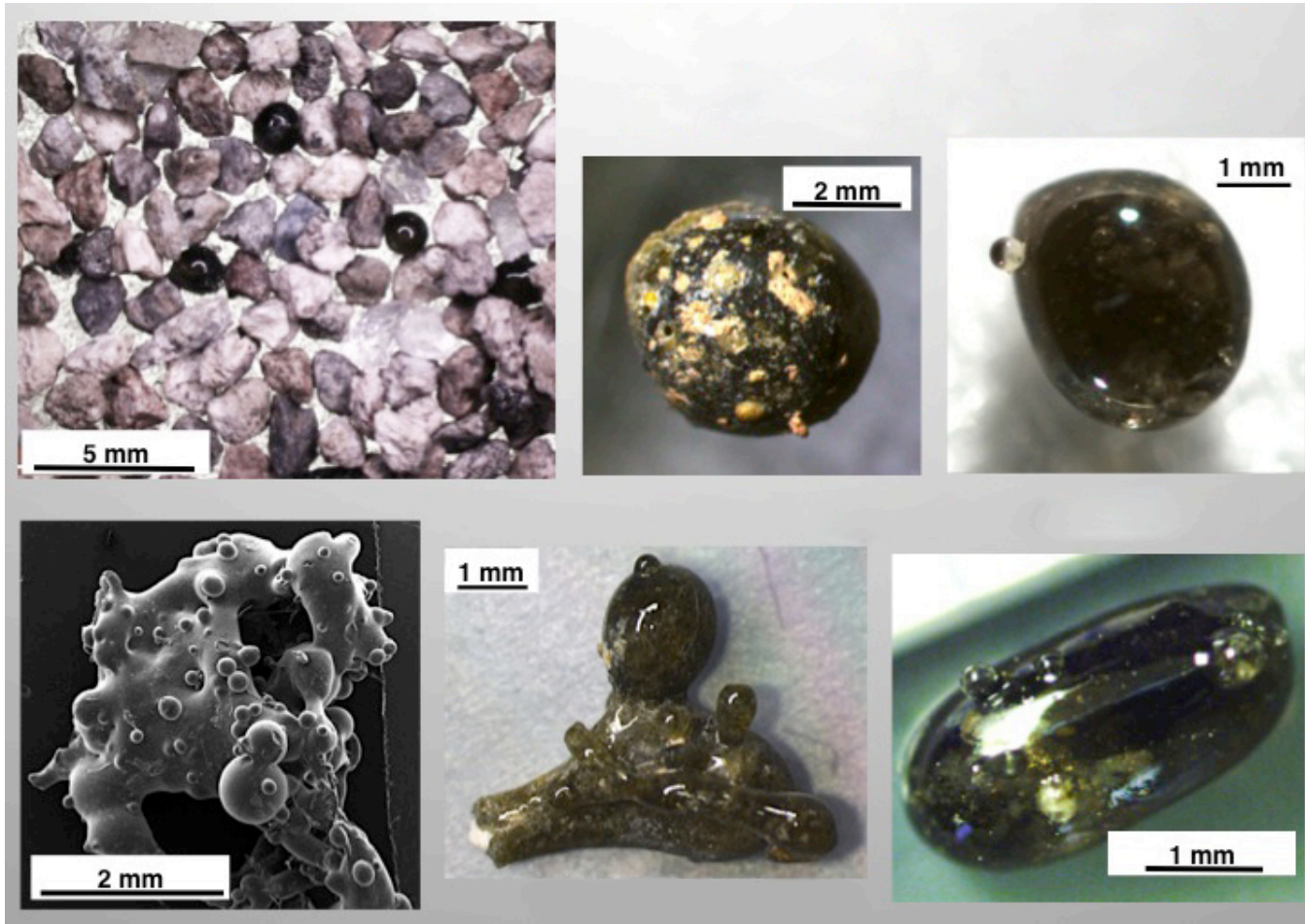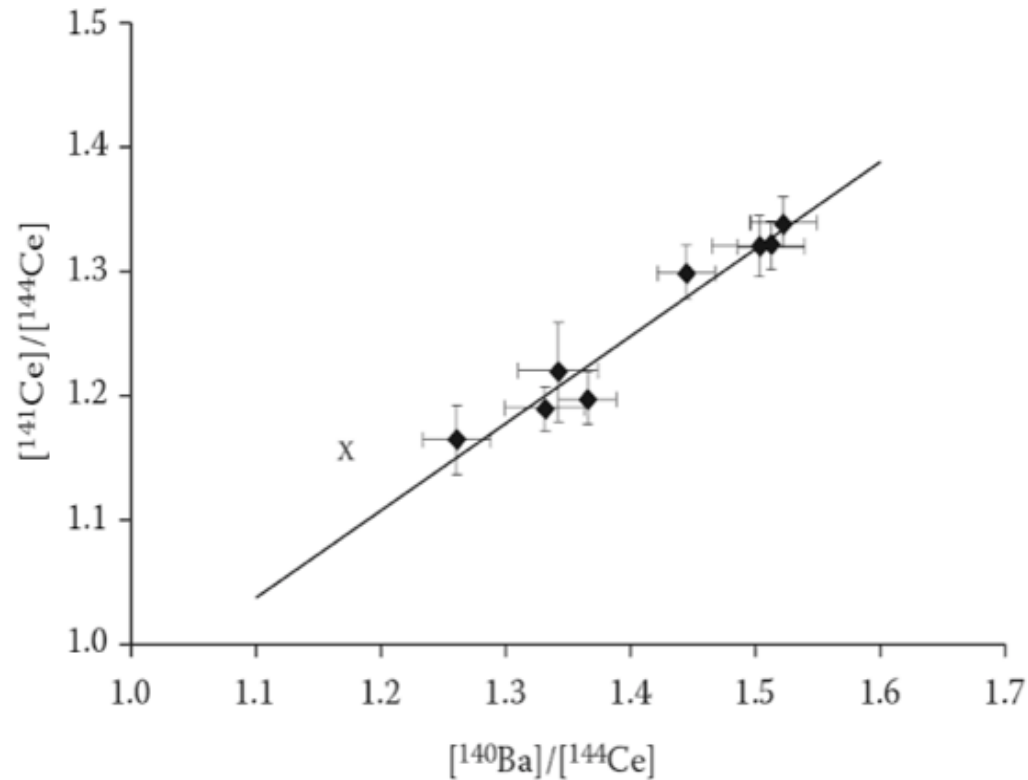

Figure 1.4: Representative dangerous fallout (DF) zone in which an early and direct threat from fallout radioactivity exists. A radiation exposure rate of 10 R/hour is used to delimit this zone.

Fallout Debris in the Near Field
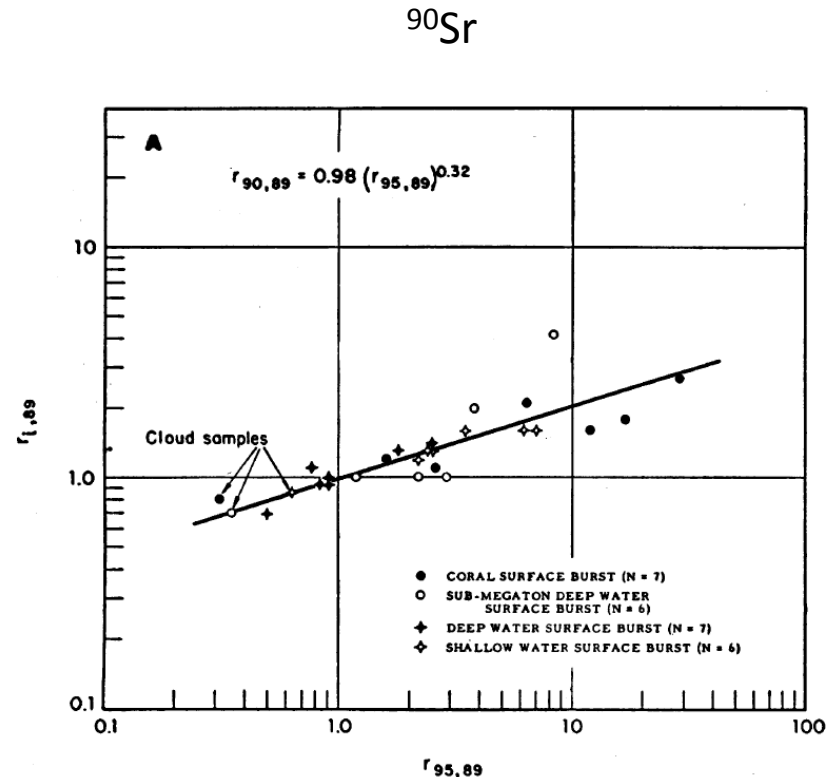
Ce-141 is Volatile?

FIGURE 5.10 A three-isotope plot used in a mixing analysis of eight samples of fractionated debris collected downrange from a 1962 nuclear test. Diamonds are the experimental data, the diagonal line is a linear fit, and "×" is the result of a calculation of homogeneous debris based on device performance.

Fission Product Volatility Depends on its Precursors
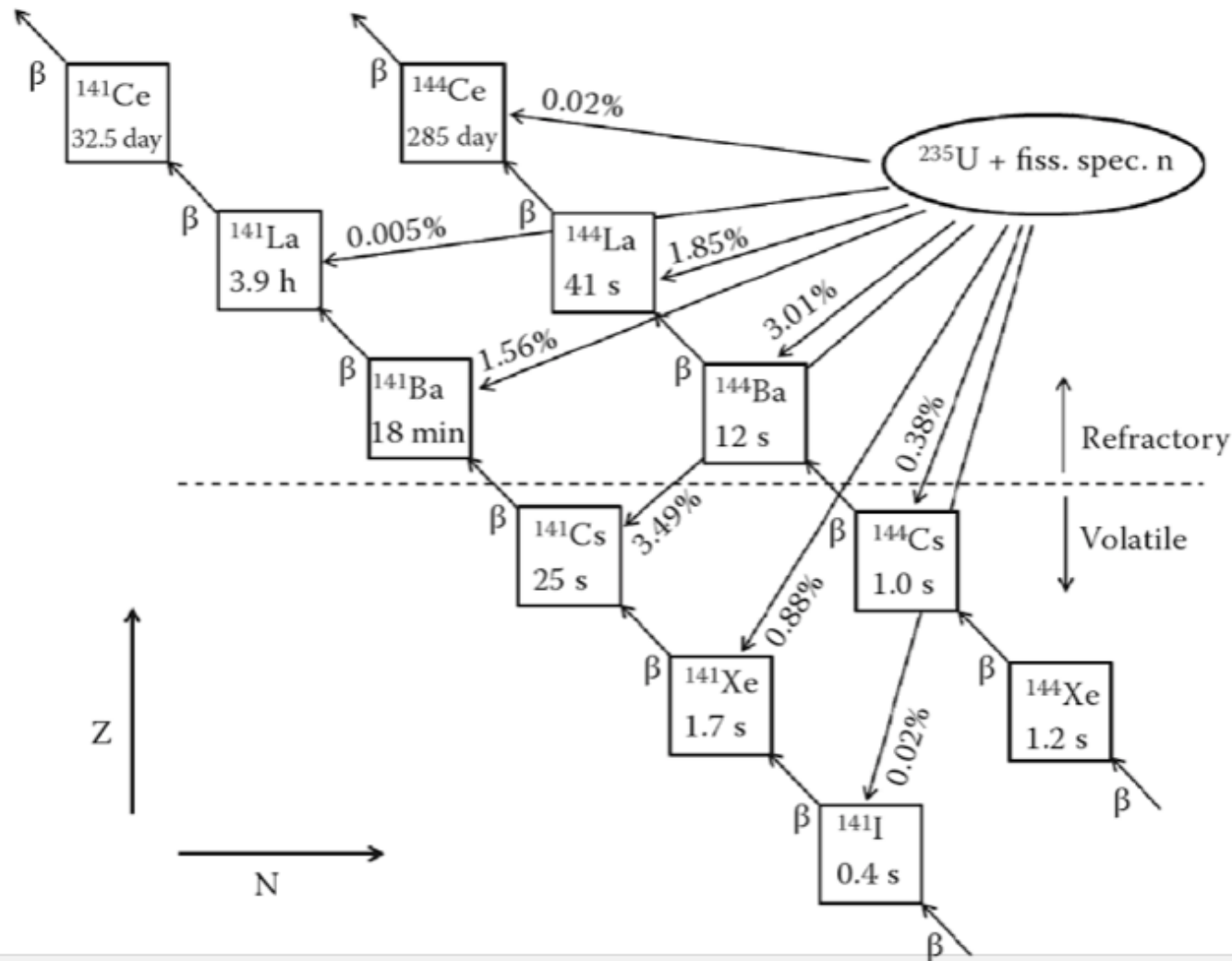
Freiling Ratios

- Science **133**, 1992(1961)

- The reference ratio of ^{95}Zr to ^{89}Sr is a measure of fractionation. The larger the ratio the more the loss of volatile species.

- The logarithmic slope nears 1.0 (linear) for refractory species.

- Logarithmic slope less than 1 indicate volatility.

^{90}Sr

A

$r_{90,89} = 0.98 \ (r_{95,89})^{0.32}$

Cloud samples

- CORAL SURFACE BURST (N = 7)
- SUB-MEGATON DEEP WATER SURFACE BURST (N = 6)
- DEEP WATER SURFACE BURST (N = 7)
- SHALLOW WATER SURFACE BURST (N = 6)

$r_{1,89}$

$r_{95,89}$

Cesium-137 is as Volatile as Strontium-89
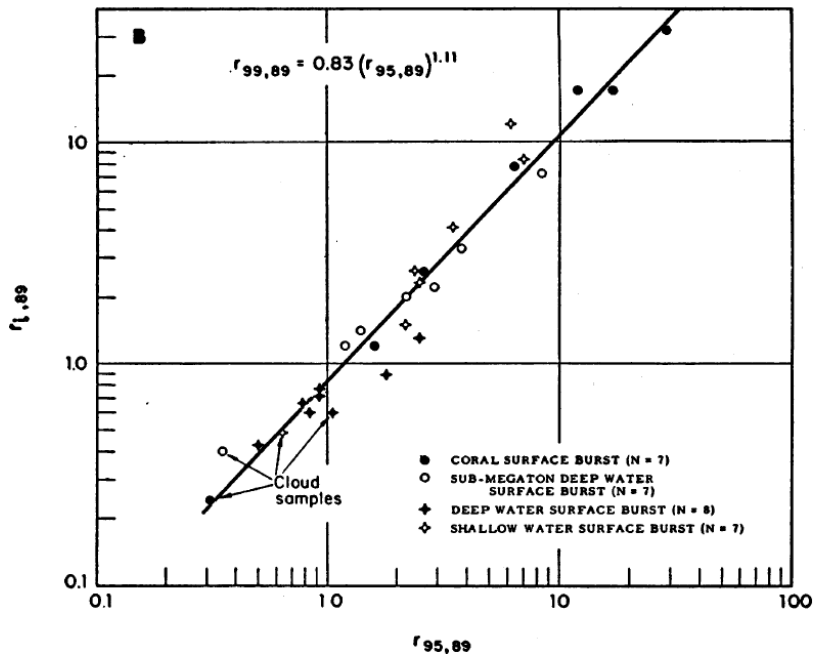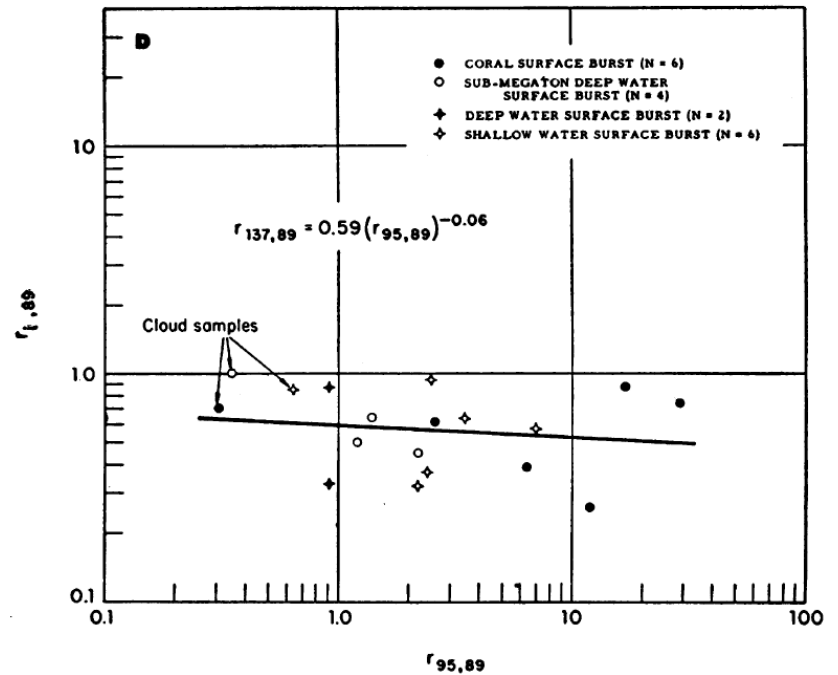
Barium-140 and Te-132 are Somewhat Volatile
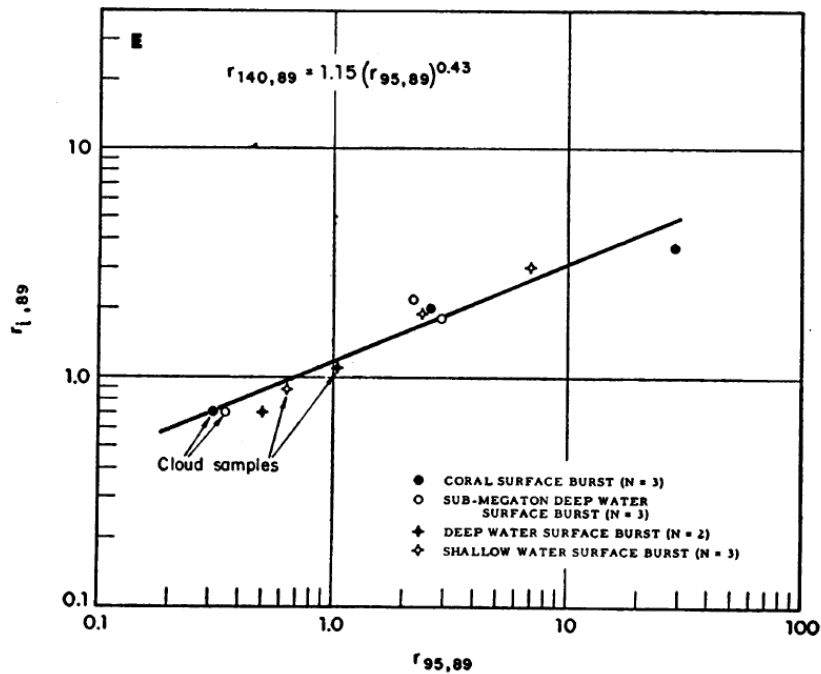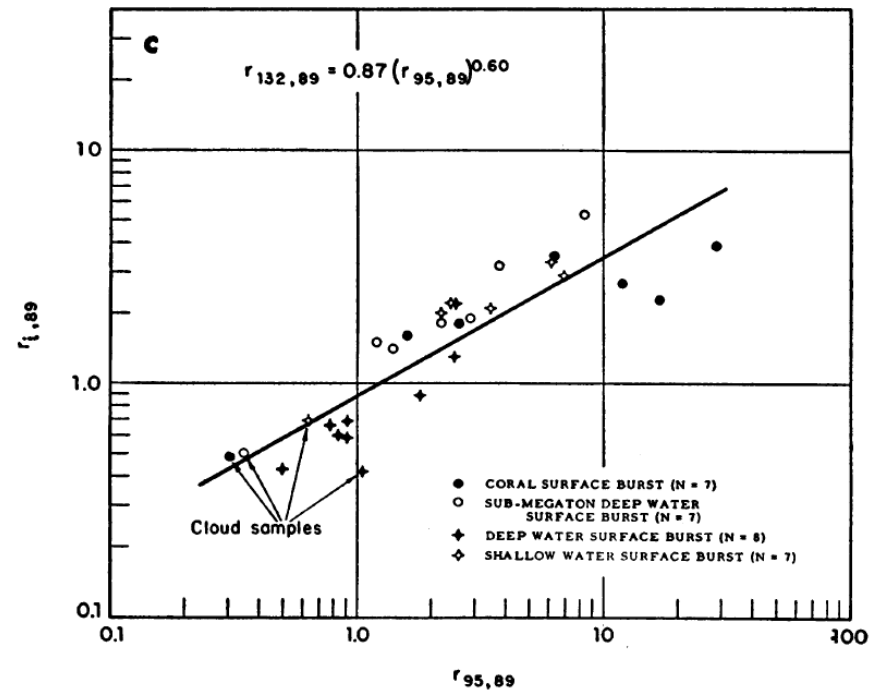
U-237 and Np-239 are Refractory

^{237}U

^{239}Np

89		Se (2 s*) $\longrightarrow$	Br (4.51 s) $\xrightarrow[88.2\%]{\nearrow^{11.8\%}}$	Kr (3.16 m) $\longrightarrow$	Rb (15.4 m) $\longrightarrow$	Sr 50.4 d)
		−, 17	37, 42	53, 34	10, 7	0, 0

n + Kr^{88} (above, reached by 11.8% branch)

90	Br (3 s*) $\longrightarrow$	Kr (33 s) $\longrightarrow$	Rb (2.7 m) $\longrightarrow$	Sr (27.7 y) $\longrightarrow$	Y (61 h)
	17, 37	57, 43	26, 20	0, 1	0, 0

95	Rb (2 s*) $\longrightarrow$	Sr (6 s*) $\longrightarrow$	Y (1 m*) $\longrightarrow$	Zr (65 d)
	26, 24	58, 44	17, 29	0, 3

Zr (65 d) $\xrightarrow{2\%}$ Nb$_1$ (90 h) 0, 0

Zr (65 d) $\xrightarrow{98\%}$ Nb$_2$ (35 d) 0, 0

99	Sr (1 s*) $\longrightarrow$	Y (1.5 s*) $\longrightarrow$	Zr (30 s) $\longrightarrow$	Nb (3.8 m) $\longrightarrow$	Mo (68 h) $\xrightarrow{13\%}$	Tc$_1$ (5.9 h)
	7, −	49, 28	40, 44	3, 26	0, 2	0, 0

132	Sn (2.5 s*) $\longrightarrow$	Sb (2.2 m) $\longrightarrow$	Te (77.7 h) $\longrightarrow$	I (2.4 h)
	5, 28	45, 44	45, 26	5, 2

137	Te (3 s*) $\longrightarrow$	I (22 s) $\xrightarrow[93.2\%]{\nearrow^{6.8\%}}$	Xe (3.9 m) $\longrightarrow$	Cs (37 y) $\xrightarrow{92\%}$	Ba$_1$ (2.64 m)
	10, 28	53, 44	33, 24	2, 2	0, 0

n (above, reached by 6.8% branch)

140	I (1.5 s*) $\longrightarrow$	Xe (16 s) $\longrightarrow$	Cs (66 s) $\longrightarrow$	Ba (12.8 d) $\longrightarrow$	La (40 h)
	7, 14	49, 41	40, 37	3, 9	0, 0

144	Cs (1.5 s*) $\longrightarrow$	Ba (3.5 s*) $\longrightarrow$	La (15 s) $\longrightarrow$	Ce (290 d) $\longrightarrow$	Pr (17.5 m)
	31, 14	56, 41	13, 36	0, 9	0, 0

237	U^{237} (7 d)

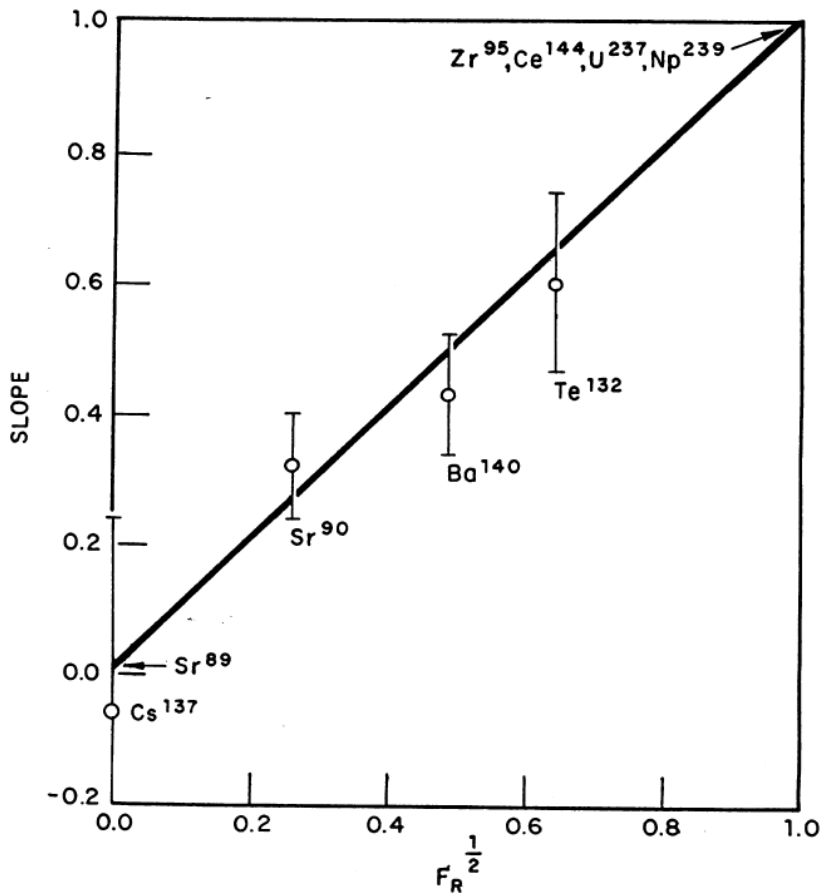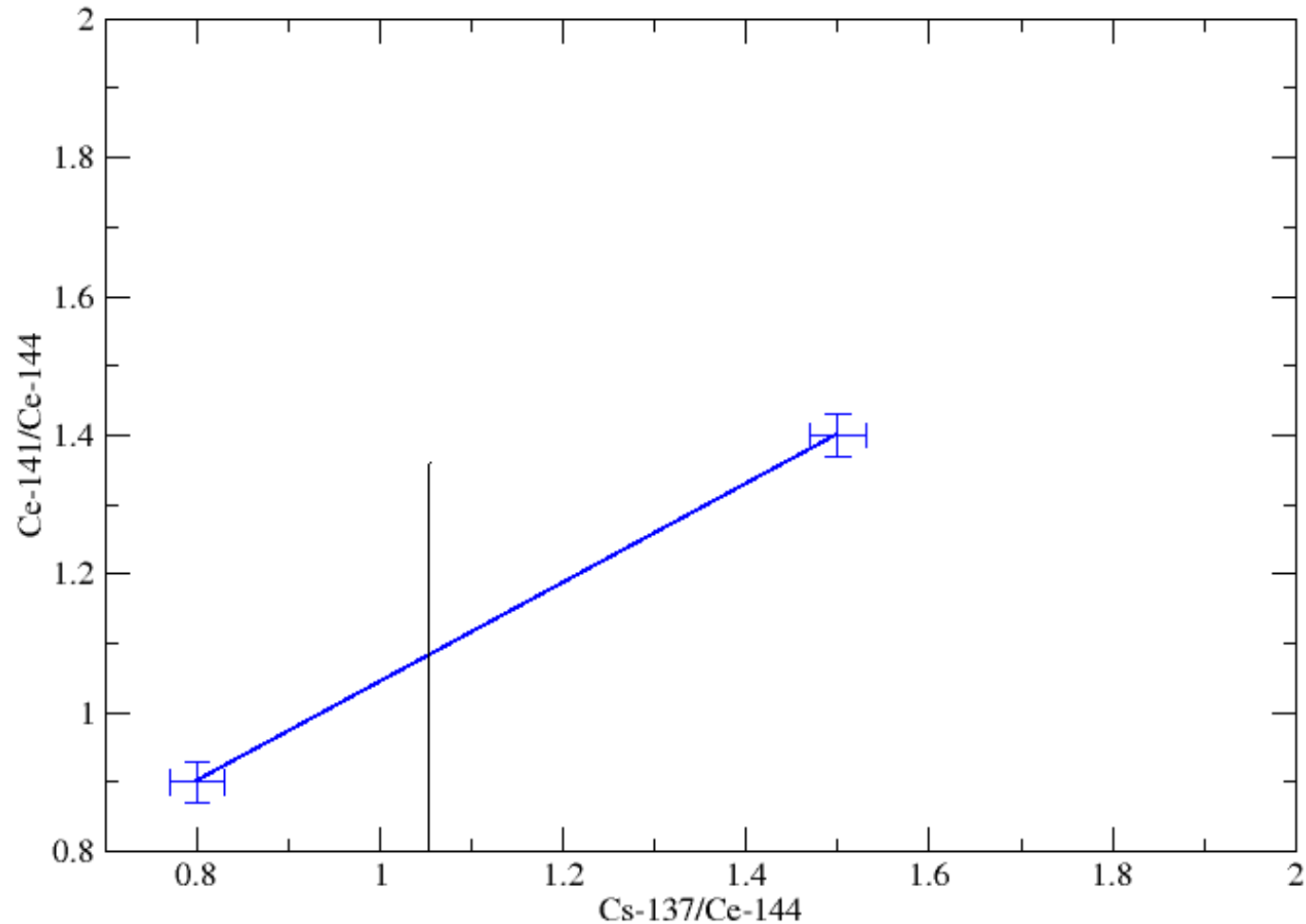| 239	U^{239} (23.5 m) $\longrightarrow$ Np^{239} (2.33 d)

Correlation of the log slope with Volatility

Fig. 3. Dependence of correlation slope on volatility of the precursor.

- The $F_r 1/2$ is the fraction of refractory precursors at 35 seconds.

- 35 seconds is approximately the time when particulates condense from the fireball.

How to Correct for Fractionation

Environmental Contamination

- If activated dirt is incorporated into the debris sample then isotopes, such as, ^{239}Np and natural uranium can contaminate the data.

- ^{160}Tb or ^{134}Cs (in excess of the independent fission yield) may be used to remove this contamination.

- Isotope ratios that trend against these contaminant isotopes can be corrected by extrapolation to zero.

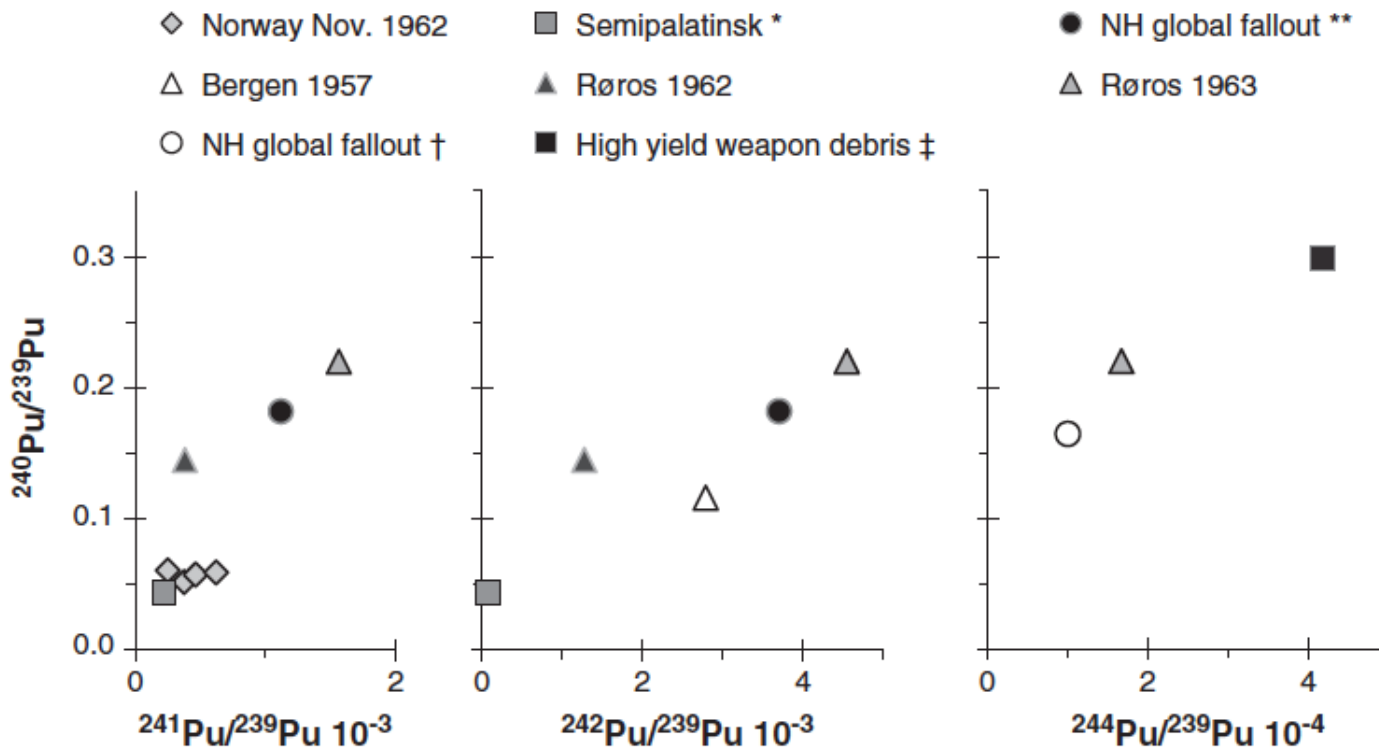# C.C. Wendel et al. / Environment International 59 (2013) 92–102

Fig. 4. Atom ratios of Pu (241Pu/239Pu, 242Pu/239Pu and 244Pu/239Pu) (vertical axes) plotted against 240Pu/239Pu (horizontal axis). Reference date 01 January 2012. The November 1962 samples were individually analysed, while the autumn and spring samples from Bergen and Røros in 1957, 1962 and 1963 respectively were based on pooled samples from each period and site. Literature data from *Beasley et al. (1998) based on measurements of soils at ground zero in Semipalatinsk; **Kelley et al. (1999) soil samples collected worldwide; †Winkler (2007) sediment profile from Lake Erie; ‡Lachner et al. (2010), mixed high yield weapon debris from the Bikini atoll.